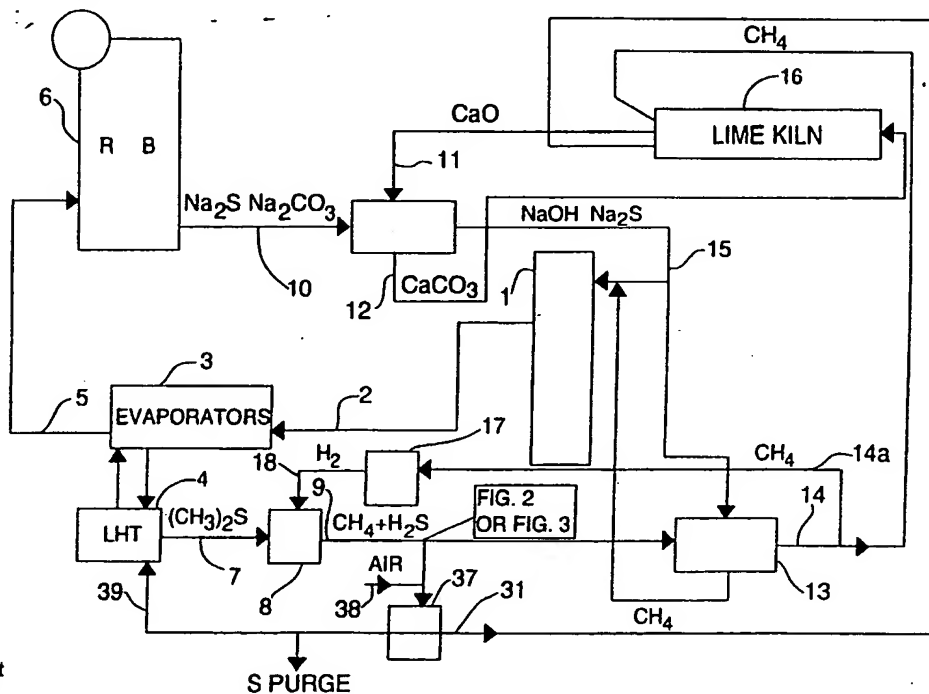


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(54) Title: A METHOD OF RECOVERING ENERGY AND CHEMICALS FROM BLACK LIQUOR



(57) Abstract

A method and apparatus for treating black liquor generated in a sulfate pulping process to recover energy and chemicals therefrom includes heating (4) the black liquor (2) at a temperature and for a time period to produce substantial volumes of off gases (7) containing organic sulfur compounds; generating hydrogen sulfide (9) and preferably methane from the off gases; and utilizing the generated hydrogen sulfide in the sulfate pulping process. The hydrogen sulfide can be absorbed (13) into white liquor (15) to selectively control the sulfur content of the white liquor. The methane (31) is used as fuel in a lime reburning kiln (16).

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ES	Spain				

-1-

1
2 **A METHOD OF RECOVERING ENERGY AND CHEMICALS FROM**
3 **BLACK LIQUOR**
4

5
6 BACKGROUND AND SUMMARY OF THE INVENTION
7

8
9 Wood is treated in sulfate cooking by white liquor
10 containing NaOH and Na₂S, whereby lignin is dissolved
11 and cellulose fibers are released. The mixture of
12 cellulose fibers (pulp) and cooking chemicals,
13 mainly containing sodium hydroxide and sodium
14 sulfide, is treated with water, whereby black
15 liquor is generated. The black liquor is
16 concentrated by evaporation. The concentrated black
17 liquor is combusted in a soda recovery boiler and
18 the chemical melt thus produced and mainly
19 containing Na₂S and Na₂CO₃ is dissolved in water,
20 whereby green liquor is generated. The green liquor
21 is causticized by caustic lime (CaO) to yield white
22 liquor containing Na₂S and NaOH. Another product of
23 the causticizing process is lime sludge mainly
24 formed by CaCO₃. White liquor is transferred to a
25 digester house and the lime sludge is calcinated in
26 a lime sludge reburning kiln to caustic lime being
27 reutilized in the causticizing.

28 Sulfur emissions are generated in a sulfate
29 cellulose mill mainly in the soda recovery boiler,
30 the evaporation plant and the digester house. In
31 order to decrease the environmental impact of the
32 sulfur the emissions thereof should be minimized.

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1 It has been noted that the increase of the dry
2 solids content of black liquor decreases the sulfur
3 emissions of a soda recovery boiler. On the other
4 hand, the sulfur content of green liquor increases
5 due to the above and thus the sulfidity of white
6 liquor as well as the sulfur content of the black
7 liquor are also increased. It can also be assumed
8 that the sulfur emissions of the evaporation plant
9 increase due to the higher sulfur content of the
10 black liquor.

11 Finnish published application 75615 (US Pat. No.
12 4,929,307) teaches that the viscosity of the black
13 liquor can be decreased by heat treating the black
14 liquor at a temperature higher than its cooking
15 temperature. Due to this it is possible to
16 evaporate black liquor to a higher dry solids
17 content, whereby the sulfur emissions of a soda
18 recovery boiler are decreased.

19 It is appreciated from US Patent 2,711,430 to heat
20 black liquor to thereby release organic sulfur
21 compounds.

22 Co-pending US Patent Application Serial No. 614,722
23 discloses a method for removing sulfur from black
24 liquor. The black liquor is heated preferably
25 before the last effect of the evaporation at a
26 temperature higher than the cooking temperature and
27 the sulfidity of white liquor is adjusted by
28 adjusting the temperature and/or retention time of
29 the heat treatment so that a desired amount of
30 sulfur compounds, such as organic sulfur compounds,
31 including mainly dimethyl sulfide and methyl
32 mercaptan, are separated from the gaseous black

-3-

1 liquor.

2 In the heat treatment of black liquor the long
3 lignin/saccharide chains are split and the methoxy
4 groups in the black liquor will form dimethyl
5 sulfide (DMS) as a byproduct. Approximately 4-6
6 weight-% of the dry solids of the black liquor can
7 potentially become gas containing dimethyl sulfide.

8

9 Surprisingly, it has been noted that the
10 above-mentioned phenomena can be utilized in a
11 completely new manner.

12

13 According to the present invention, a method is
14 provided for treatment of black liquor generated in
15 a sulfate pulping process to recover energy and
16 chemicals therefrom, in which method

17 (a) the black liquor is heated at a temperature and
18 for a time period such that substantial volumes of
19 off gases containing organic sulfur compounds are
20 produced;

21 (b) generating methane and hydrogen sulfide from at
22 least a part of the off gases; and

23 (c) utilizing the generated hydrogen sulfide in the
24 sulfate pulping process.

25 The apparatus according to the present invention
26 comprises

27 means for heating the black liquor for a period of
28 time so as to generate off gases containing organic
29 sulfur compounds;

30 means connected to the heating means for generating
31 hydrogen sulfide from the organic sulfur compounds
32 contained in the off gases;

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1 means connected to the hydrogen
2 sulfide generating means for controlling the
3 sulfidity of white liquor and for separating the
4 methane from the hydrogen sulfide by selectively
5 passing the methane and the hydrogen sulfide into
6 contact with the white liquor; and

7 means connected to the sulfidity
8 control means for feeding the white liquor of
9 controlled sulfidity to the cooking stage of a
10 sulfate pulping process.

11
12 The generated hydrogen sulfide can be
13 separated from the gas stream by absorption in NaOH
14 solution or in white liquor prior to the cooking
15 stage. Thus it is possible to increase and control
16 the sulphidity of white liquor. This is very
17 advantageous, because a higher sulfide concentration
18 in white liquor produces kraft pulp with a higher
19 viscosity and better physical properties.

20 Alternatively, the H_2S can be absorbed in
21 an amine absorber or similar device. An alternative
22 to absorption is separation by compression and
23 successive partial condensation. The hydrogen
24 sulfide separated can be used for many purposes, for
25 instance, it can be converted into elementary sulfur
26 in a process similar to the Claus process. The
27 sulfur formed is fed back into the heat treatment
28 reactor, in which the black liquor is treated, to
29 enhance the formation of new dimethyl sulfide or the
30 sulfur is purged from the system as crystalline
31 sulfur.

32 The produced H_2S can be used in the pulping

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1 process to considerably improve the pulping yield by
2 pre-impregnation of H_2S into the wood-chips before
3 the alkaline delignification process. Preferably
4 the off gases are treated in such a way that in
5 addition to hydrogen sulfide methane is also
6 produced. The methane produced can be used, for
7 instance, to substitute the fuel normally used in
8 the lime reburning operation. A part of the off
9 gases can, if required, be treated in such a way
10 that other compounds than hydrogen sulfide are
11 produced, for example, sulfur dioxide. By means of
12 the present method the removal of the sulfur from
13 the black liquor and the recycling of the sulfur in
14 the kraft liquor recovery process are improved. A
15 substantial portion of sulfur can bypass the soda
16 recovery boiler and the sulfur recovered can be
17 returned to the pulping process, for instance, to
18 cooking liquors.

19 It is now also possible to partially
20 convert black liquor to usable fuel, which can be
21 used in pulping operations, e.g. in lime kilns, or
22 outside such operations. It can also be used in a
23 separate superheater of the soda recovery boiler or
24 in other boilers.

25 When sulfur is separated from black
26 liquor, in the manner described, before it is
27 supplied to the soda recovery boiler, the dry solids
28 flow flowing into the boiler can decrease by about
29 10% (corresponding to an increase in throughput of
30 the recovery boiler by about 10%) and, at the same
31 time, the net heat content of the black liquor is
32 reduced. In other words, the load of the boiler as

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1 well as the amount of sulfur to be processed are
2 decreased.

3 By adjusting the temperature and/or
4 retention time of the heat treatment it is possible
5 to adjust the amount of the dimethyl sulfide and
6 other organic sulfur compounds exiting from the
7 black liquor. The formation of dimethyl sulfide can
8 be adjusted also by feeding sulfur to the heat
9 treatment reactor.

10 The heat treatment is carried out as
11 pressure heating at a temperature of approximately
12 170-350°C, preferably higher than 190°C, and more
13 preferably between 190 and 290°C. The treatment
14 time depends on the temperature and the quality of
15 the liquor. The retention time is typically about
16 1-60 minutes in order to generate gas including
17 sulfur compounds to a significant extent. The
18 treatment can always be carried out when the removal
19 of sulfur from black liquor is desired. Preferably,
20 the treatment is carried out prior to the final
21 evaporation.
22

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BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described below by way of example with reference to the accompanying drawings, in which:

FIG. 1 is a schematic diagram illustrating the method of improving the utilization of sulfur compounds in the kraft pulping process in accordance with the present invention;

FIG. 2 is a diagram illustrating a method for separating hydrogen sulfide from methane in the method of FIG. 1; and

FIG. 3 is another schematic illustration of yet a further method for separating hydrogen sulfide from methane in the method of FIG. 1.

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1 DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED
2 EMBODIMENTS

3
4 In Fig. 1 the weak black liquor is fed
5 from a digester house 1 through line 2 to, and is
6 evaporated in, for instance, a multiple effect
7 evaporating system 3 in accordance with US Patent
8 4,953,607 the entire disclosure of which is hereby
9 incorporated by reference. The lignin in the liquor
10 to be evaporated is split by a heat treatment, that
11 is, by heating the black liquor under pressure for
12 a predetermined time, in a reactor vessel 4, whereby
13 gases containing organic sulfur compounds are
14 generated. At temperatures over 200°C the amount of
15 sulfur exiting from the black liquor can be 30-65%
16 of all sulphur contained in the black liquor. The
17 heat treatment is carried out under water pressure,
18 i.e. at pressures varying from about 8 bars to 165
19 bars, preferably from about 12 bars to 80 bars.
20 Suitable temperatures for the heat treatment range
21 from about 170-350°C and preferably from 190-290°C.
22 At these temperatures substantially all of the
23 organic sulfur compounds, which are formed in the
24 black liquor during the heat treatment, are
25 liberated in form of gas. For example, at a
26 temperature of 280°C this gas contains about 65%
27 dimethyl sulfide, about 34% methyl mercaptan and 1%
28 hydrogen sulfide.

29 The objective of the pressure heating is,
30 on one hand, to decrease the viscosity of the black
31 liquor to be concentrated thereby improving the
32 evaporation and treatment abilities of the liquor,

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1 and, on the other hand, to remove sulfur therefrom.
2 The heat treatment causes the splitting of the
3 lignin in the black liquor, which, in turn, results
4 in a decrease of the viscosity thereof. At the same
5 time methoxy groups of lignin split off, thereby
6 generating dimethyl sulfide (DMS).

7 The concentrated black liquor is
8 transferred through line 5 to a soda recovery boiler
9 6 for combustion therein. The chemical melt thus
10 produced and mainly containing Na_2S and Na_2CO_3 is
11 dissolved in water, whereby green liquor in line 10
12 is generated. The green liquor is thereafter
13 causticized in a suitable vessel with lime (CaO)
14 added through line 11 to form white liquor exiting
15 through line 15, and which is transferred to the
16 digester 1 or for further treatment. The lime mud
17 also formed during the causticizing step is fed
18 through line 12 into a lime kiln to be calcined
19 therein to recover the lime therefrom.

20 Dimethyl sulfide (DMS) formed during the
21 above described heat treatment of the black liquor
22 in reactor vessel 4 is fed through line 7 into
23 hydroconverter 8 and reduced therein to methane and
24 hydrogen sulfide. This reduction of DMS is achieved
25 with H_2 or $\text{CO} + \text{H}_2$ at a temperature of about 300°C .
26 H_2S can be separated from the gas mixture (CH_4 and
27 H_2S) contained in line 9 by absorption thereof in a
28 white liquor scrubber 13, whereby a substantially
29 sulfur-free CH_4 gas is produced. H_2S reacts with
30 NaOH as follows: $2 \text{CH}_4 + \text{H}_2\text{S} + 2\text{NaOH} \rightarrow \text{Na}_2\text{S} + 2\text{CH}_4$
31 $+ 2\text{H}_2\text{O}$.

32 Because sulfur is removed from the black

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1 liquor prior to the soda recovery boiler, the sulfur
2 content of white liquor produced from this liquor is
3 lower than that of white liquor normally used in
4 cooking. The white liquor having low sulfur content
5 in line 15 can be used in the later stages of
6 cooking. As mentioned above, a portion of white
7 liquor is added into scrubber 13 through line 15a,
8 where it absorbs the sulfur compounds and the sulfur
9 content thereof increases. Preferably it is then
10 transferred through line 15b to the upper part of
11 the digester 1 to increase the sulfidity and thus
12 improve the pulp yield and pulp quality. A higher
13 white liquor sulfidity is preferred at the beginning
14 of cooking than in the later stages. For example,
15 by maintaining the same viscosity value with the
16 present method as with conventional method it is
17 possible to decrease the previously obtained kappa
18 number by 5.

19 A portion of the methane gas is fed
20 through line 14 to a lime kiln 16 to substitute the
21 fuel normally used therein. Another portion of the
22 methane is fed through line 14a, after the white
23 liquor scrubber, to a converter 17 and is converted
24 therein to carbon monoxide and hydrogen through
25 sub-stoichiometric combustion, which is a
26 conventional method. The hydrogen and carbon
27 monoxide 18 are fed to hydroconverter 8 to be used
28 therein to reduce the dimethyl sulfide to methane
29 and hydrogen sulfide.

30 Alternatively to absorbing the hydrogen
31 sulfide as described, the H_2S can also be separated
32 by compression and partial condensation as

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1 illustrated in Fig. 2. The gas mixture containing
2 methane and hydrogen sulfide is compressed in a
3 pressure apparatus 20 to a pressure of at least 20
4 bar and partially condensed in condenser 21 so that
5 most of the hydrogen sulfide 22 is separated from
6 the methane. The produced H_2S exiting therefrom
7 through line 22 can be used in the pulping process
8 to considerably improve the pulping yield by
9 pre-impregnating the wood-chips with H_2S before the
10 alkaline delignification process. The production
11 increase based on fiber production is at least
12 10-12%. The remainder of the gas mixture is
13 transferred through line 12 to an absorber 23 and
14 absorbed therein using methanol as an absorbent,
15 thereby separating the remaining hydrogen sulfide
16 from the methane. The free methane gas in line 25
17 can then be used in the lime kiln as fuel as
18 described above.

19 Alternatively the gas mixture containing
20 methane and hydrogen sulfide after the hydrogen
21 converter 8 can also be treated by absorption as
22 follows. The hydrogen sulfide is separated from the
23 methane by absorbing it into an amine solution
24 containing methylamine in an amine scrubber 30 as
25 illustrated in Fig. 3. The methane exiting from the
26 scrubber is transferred through line 31 to the lime
27 kiln 16 to be used as a fuel. The amine solution
28 containing the hydrogen sulfide is transferred
29 through line 32 to an amine stripper 34, wherein the
30 hydrogen sulfide is separated by the addition of
31 steam. The amine solution in line 35 which is free
32 from H_2S is fed back to scrubber 30 through a heat

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1 exchanger 33, in which the solution coming from the
2 scrubber is preheated. The hydrogen sulfide exiting
3 from the stripper 34 through line 36 can be utilized
4 as described earlier.

5 Further, a part or the entire flow of
6 hydrogen sulfide can be oxidized to elementary
7 sulfur according to processes similar to the Claus
8 process, such as the method described in US Patent
9 No. 4,919,914 which is also incorporated herein in
10 its entirety by reference. Also, the gas mixture in
11 line 9 after the hydroconverter 8 can be treated by
12 this method. This method is based on the principle
13 of using Fe as a catalyst to convert H_2S to S and H_2O
14 in a flotation cell. The hydrogen sulfide
15 containing gas stream in line 9 (Fig. 1) is
16 continuously fed to a reaction zone in an agitated
17 flotation cell 37 which contains an aqueous medium
18 and as a hydrogen sulfide oxidizing catalyst,
19 chelatic ferric hydroxide dissolved in the aqueous
20 medium. A separate oxygen-containing gas stream,
21 usually air is continuously fed through line 38 to
22 the reaction medium. The process proceeds according
23 to the reaction: $H_2S + 1/2 O_2 \rightarrow H_2O + S$. The sulfur
24 particles which are formed in the oxidation reaction
25 are continuously transported to the surface of the
26 aqueous medium from which the sulfur can easily be
27 recovered. The sulfur formed is fed back through
28 line 39 to the heat treatment reactor 4 to enhance
29 the formation of new dimethyl sulfide or is
30 withdrawn from the system as crystalline sulfur. If
31 the gas mixture contained methane, the methane is
32 separated therefrom and transferred to the lime kiln

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1 through line 31.

2 It should be understood that the preferred
3 embodiments and examples described are for
4 illustrative purposes only and are not to be
5 construed as limiting the scope of the present
6 invention which is properly delineated only in the
7 appended claims.
8

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CLAIMS

What is claimed is:

1. A method of treating black liquor generated in a sulfate pulping process to recover energy and chemicals therefrom, characterized in that

(a) the black liquor is heated at a temperature and for a time period such that substantial volumes of off gases containing organic sulfur compounds are produced;

(b) generating hydrogen sulfide from the off gases; and

(c) utilizing the generated hydrogen sulfide in the sulfate pulping process.

2. The method in accordance with claim 1, further characterized in that in step (b) hydrogen sulfide and methane are generated.

3. The method in accordance with claim 1 or 2, further characterized in that step (c) is practiced by bringing the generated hydrogen sulfide into contact with white liquor, and then using the white liquor in the sulfate pulping process.

4. The method in accordance with claim 1 or 2, characterized by the further step of converting some of the hydrogen sulfide from step (b) into elementary sulfur.

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1 5. The method in accordance with claim
2 4, characterized in that the black liquor heating is
3 practiced in a heat treatment reactor, and the
4 sulfur is fed back to said heat treatment reactor
5 vessel to enhance the formation of dimethyl sulfide
6 therein.

7
8 6. The method according to claim 1,
9 further characterized in that the black liquor
10 heating is practiced at a temperature of about
11 170-350° C, preferably at about 190-290° C, for a
12 time period of about 1-60 minutes.

13
14 7. The method in accordance with claim
15 2, further characterized by the step (d) of
16 separating the hydrogen sulfide from the methane.

17
18 8. The method according to claim 7
19 further characterized in that steps (c) and (d) are
20 practiced by passing a mixture of methane and
21 hydrogen sulfide into contact with white liquor to
22 absorb the hydrogen sulfide into the white liquor to
23 selectively control the sulfur content of the white
24 liquor, and then using the white liquor in a sulfate
25 cooking step.

26
27 9. The method according to claim 7
28 further characterized in that step (d) is practiced
29 by compression and successive partial condensation,
30 or by absorbing the hydrogen sulfide in an amino
31 absorber.

32

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1 10. The method according to claim 7,
2 wherein the pulping process includes a lime
3 reburning kiln; and the methane from step (d) is
4 utilized as fuel in the lime reburning kiln.
5

6 11. The method according to claim 2,
7 characterized in that step (b) is practiced in a
8 hydroconverter.
9

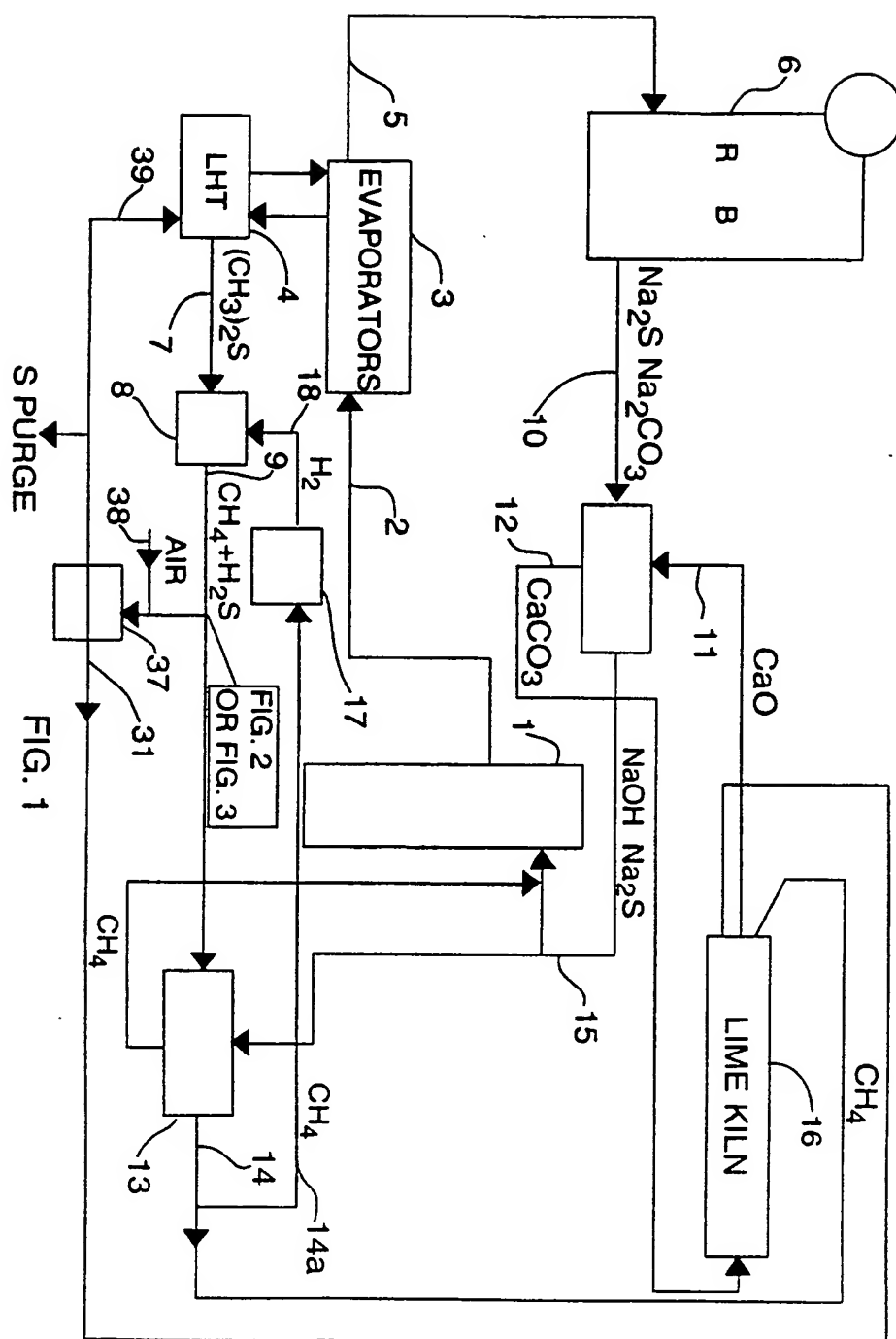
10 12. Apparatus for utilizing black liquor
11 from a sulfate pulping process comprising:

12 means for heating the black liquor for a
13 period of time so as to generate off gases
14 containing organic sulfur compounds;

15 means connected to the heating means for
16 generating hydrogen sulfide from the organic sulfur
17 compounds contained in the off gases;

18 means connected to the hydrogen sulfide
19 generating means for controlling the sulfidity of
20 white liquor and for separating the methane from the
21 hydrogen sulfide by selectively passing the methane
22 and hydrogen sulfide into contact with the white
23 liquor; and

24 means connected to the sulfidity control
25 means for feeding the white liquor of controlled
26 sulfidity to the cooking stage of a sulfate pulping
27 process.

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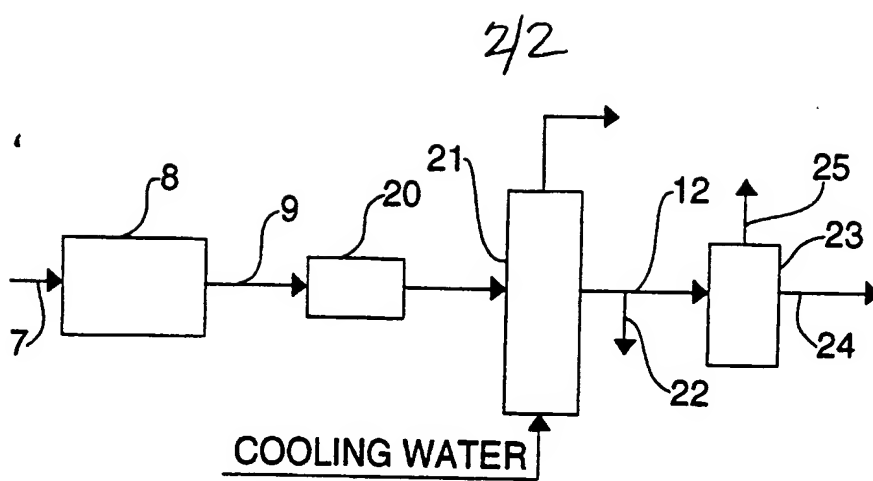


FIG. 2

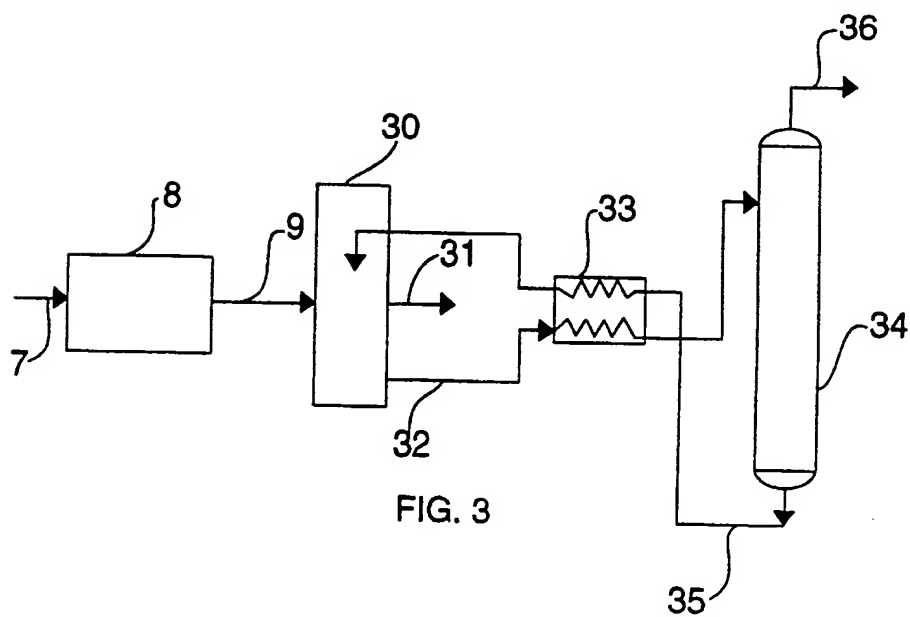


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/00021

I. CLASSIFICATION OF SUBJECT MATTER		
IPC(5): D21C 11/00, 11/06, 11/14 U.S. CL.: 162/30.11; 423/207,563, DIGEST 3		
FIELDS SEARCHED		
U.S. 423/206R, 207,228,563, DIGEST 3; 162/30.1, 30.11, 31, 34; 208/209; 585/733		
Documentation Searched other than Minimum Documentation to the extent that such documents are included in the fields searched		
II. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages *	Relevant to Claim No. *
X	US, A, 3,762,989 (TIMPE) 02 October 1973, See column 3, lines 15; column 6 line 45, column 9, lines 40-60	1-12
A	US, A, 3,718,446 (BRINK ET AL.) 27 February 1973.	4,7,9
A	US, A, 3,607,619 (HESS ET AL.) 21 September 1971, See column 2, lines 65-75.	1-12
Y	US, A, 4,431,617 (FARIN) 14 February 1984, See claim 1.	3,8
A	US, A, 3,944,462 (HESS ET AL.) 16 March 1976.	1-12
A	US, A, 4,851,600 (LOUW) 25 July 1990.	1-12
<p>* Special categories of cited documents: 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
23 JUNE 1992	14 JUL 1992	
International Searching Authority	Signature of Authorized Officer	
ISA/US	GARY P. STRAUB	
	REGULATORY DIVISION	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 4,373,109 (OLAH) 08 February 1983.	1-12
A	US, A, 4,513,164 (OLAH) 23 April 1985.	1-12
A	US, A, 4,929,307 (KIISHILA ET AL.) 29 May 1990.	1-12
A	US, A, 4,953,607 (ERKKI ET AL.) 04 September 1990.	1-12
A	US, A, 4,919,914 (SMITH ET AL.) 24 April 1990.	4,7

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____ because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out (3), specifically:

3. ☐ Claim numbers _____ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

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